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02358021.0

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Anmeldung Nr:  
Application no.: 02358021.0  
Demande no:

Anmeldetag:  
Date of filing: 29.08.02  
Date de dépôt:

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Supported polymerisation catalysts

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)  
revendiquée(s)  
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/  
Classification internationale des brevets:

C08F10/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of  
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

### **SUPPORTED POLYMERISATION CATALYSTS**

The present invention relates to supported catalysts suitable for the polymerisation of olefins and in particular to supported metallocene catalysts providing advantages for operation in gas phase processes.

In recent years there have been many advances in the production of polyolefin  
5 homopolymers and copolymers due to the introduction of metallocene catalysts. Metallocene catalysts offer the advantage of generally a higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single site in nature. There have been developed several different families of metallocene complexes. In  
10 earlier years catalysts based on bis (cyclopentadienyl) metal complexes were developed, examples of which may be found in EP 129368 or EP 206794. More recently complexes having a single or mono cyclopentadienyl ring have been developed. Such  
complexes have been referred to as 'constrained geometry' complexes and examples of these complexes may be found in EP 416815 or EP 420436. In both of these complexes the metal atom eg. zirconium is in the highest oxidation state.

15 Other complexes however have been developed in which the metal atom may be in a reduced oxidation state. Examples of both the bis (cyclopentadienyl) and mono (cyclopentadienyl) complexes have been described in WO 96/04290 and WO 95/00526 respectively.

20 The above metallocene complexes are utilised for polymerisation in the presence of a cocatalyst or activator. Typically activators are aluminoxanes, in particular methyl aluminoxane or compounds based on boron compounds. Examples of the latter are borates such as trialkyl-substituted ammonium tetraphenyl- or tetrafluorophenyl-

borates. Catalyst systems incorporating such borate activators are described in EP 561479, EP 418044 and EP 551277.

The above metallocene complexes may be used for the polymerisation of olefins in solution, slurry or gas phase. When used in the gas phase the metallocene complex and/or the activator are suitably supported. Typical supports include inorganic oxides eg. silica or polymeric supports may alternatively be used.

Examples of the preparation of supported metallocene catalysts for the polymerisation of olefins may be found in WO 94/26793, WO 95/07939, WO 96/00245, WO 96/04318, WO 97/02297 and EP 642536.

WO 98/27119 describes supported catalyst components comprising ionic compounds comprising a cation and an anion in which the anion contains at least one substituent comprising a moiety having an active hydrogen. In this disclosure supported metallocene catalysts are exemplified in which the catalyst is prepared by treating the aforementioned ionic compound with a trialkylaluminium compound followed by subsequent treatment with the support and the metallocene.

WO 98/27119 also describes a method for activating a substantially inactive catalyst precursor comprising (a) an ionic compound comprising a cation and an anion containing at least one substituent comprising a moiety having an active hydrogen, (b) a transition metal compound and optionally, (c) a support by treatment with an organometallic compound thereby forming an active catalyst.

Various methods have been utilised to prepare supported catalysts of this type. For example WO 98/27119 describes several methods of preparing the supported catalysts disclosed therein in which the support is impregnated with the ionic compound. The volume of the ionic compound may correspond from 20 volume percent to greater than 200 volume percent of the total pore volume of the support. In a preferred preparative route the volume of the solution of the ionic compound does not exceed substantially, and is preferably equal to, the total pore volume of the support. Such methods of preparation may be referred to as incipient precipitation or incipient wetness techniques.

Recently Macromolecular Rapid Communications 2001, 22, 1427-1431 described the preparation of supported metallocene catalysts by impregnating up to the pore volume of a silica support with a premixed 1-hexene solution of co- and pro-

catalysts. Exemplified systems were silica supported bis(cyclopentadienyl) zirconium dichloride/methyl aluminoxane for slurry polymerisation. Such systems however showed no long term storage stability and after a few days were inactive for polymerisations.

5 We have now surprisingly found that the addition of a polymerisable monomer to the support prior to contact with one or both of the polymerisation catalyst and the cocatalyst results in an improved supported catalyst system which is stable over extended periods of time.

10 Thus according to the present invention there is provided a method for the preparation of a supported polymerisation catalyst system said method comprising the combination of

- (i) a porous support
- (ii) a polymerisable monomer,
- (iii) a polymerisation catalyst, and
- 15 (iv) a cocatalyst,

*characterised* in that the polymerisable monomer is added to the porous support before addition of one or both of the polymerisation catalyst and the cocatalyst.

A preferred method according to the present invention comprises the following steps:

- 20 (i) addition of a cocatalyst to a porous support,
- (ii) addition of a polymerisable monomer, and
- (iii) addition of a polymerisation catalyst.

Other suitable orders of addition according to the present invention include the following:

- 25 support, polymerisation catalyst, monomer and cocatalyst
- support, monomer, cocatalyst and polymerisation catalyst.

In the preferred embodiment the polymerisable monomer is added to the porous support at less than or equal to the pore volume of the support.

- 30 The polymerisable monomer is preferably added in liquid form either neat or as a solution.

Suitable porous support materials include inorganic metal oxides or alternatively polymeric supports may be used for example polyethylene, polypropylene, clays,

zeolites, etc.

The most preferred support material for use with the supported catalysts according to the method of the present invention is silica. Suitable silicas include Crosfield ES70 and Davison 948 silicas.

5       The support material may be subjected to a heat treatment and/or chemical treatment to reduce the water content or the hydroxyl content of the support material. Typically chemical dehydration agents are reactive metal hydrides, aluminium alkyls and halides. Prior to its use the support material may be subjected to treatment at 100°C to 1000°C and preferably at 200 to 850°C in an inert atmosphere under reduced  
10       pressure.

The support material may be further combined with an organometallic compound preferably an organoaluminium compound and most preferably a trialkylaluminium compound in a dilute solvent.

15       The support material is pretreated with the organometallic compound at a temperature of -20°C to 150°C and preferably at 20°C to 100°C.

Polymerisable monomers suitable for use in the method of the present invention include ethylene, propylene, 1-butene, 1-hexene, 1-octene, styrene, butadiene, and polar monomers for example vinyl acetate, methyl methacrylate, etc. Preferred monomers are ethylene, propylene, 1-butene or 1-hexene.

20       Alternatively a combination of one or more monomers may be used for example ethylene/1-hexene.

The polymerisable monomer is suitably used in liquid form or alternatively may be used in a suitable solvent.

25       When using a liquid monomer it may be advantageous that the catalyst components be optionally present in a solution of the polymerisable monomer for example when using 1-hexene as solvent.

The polymerisation catalyst component according to the present invention may suitably be a metallocene complex but other polymerisation catalysts typically used in conjunction with a porous support in the present of a cocatalyst may be suitable.

30       The metallocene complex may comprise for example a traditional bis(cyclopentadienyl) metallocene complex or more preferably a monocyclopentadienyl complex having a 'constrained geometry' configuration.

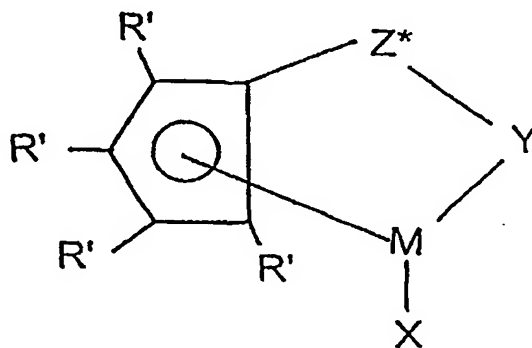
Bis(cyclopentadienyl) metallocene complexes may be represented by those disclosed in EP 129368 or EP 206794. Such complexes may be unbridged eg. bis(cyclopentadienyl) zirconium dichloride or bridged eg. ethylene bis(indenyl) zirconium dichloride. Other suitable metallocene complexes are those

5 bis(cyclopentadienyl) diene complexes described in WO 96/04290.

Examples of monocyclopentadienyl complexes suitable for use in the present invention are described in EP 416815, EP 418044, EP 420436 and EP 551277.

Particularly suitable monocyclopentadienyl complexes are those disclosed in WO 95/00526 the disclosure of which is incorporated herein by reference.

10 Preferred metallocene complexes for use in the preparation of the supported catalysts of the present invention may be represented by the general formula:



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

15

X is a neutral  $\eta^4$  bonded diene group having up to 30 non-hydrogen atoms, which forms a  $\pi$  complex with M;

20

Y is -O-, -S-, -NR\*-, -PR\*-,

M is titanium or zirconium in the + 2 formal oxidation state;

Z\* is SiR\*<sub>2</sub>, CR\*<sub>2</sub>, SiR\*<sub>2</sub>SIR\*<sub>2</sub>, CR\*<sub>2</sub>CR\*<sub>2</sub>, CR\*=CR\*, CR\*<sub>2</sub>SIR\*<sub>2</sub>, or

GeR\*<sub>2</sub>, wherein:

R\* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said

5 R\* having up to 10 non-hydrogen atoms, and optionally, two R\* groups from Z\* (when R\* is not hydrogen), or an R\* group from Z\* and an R\* group from Y form a ring system.

Examples of suitable X groups include s-trans- $\eta^4$ -1,4-diphenyl-1,3-butadiene, s-trans- $\eta^4$ -3-methyl-1,3-pentadiene; s-trans- $\eta^4$ -2,4-hexadiene; s-trans- $\eta^4$ -1,3-pentadiene; s-trans- $\eta^4$ -1,4-ditolyl-1,3-butadiene; s-trans- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene; s-  
10 cis- $\eta^4$ -3-methyl-1,3-pentadiene; s-cis- $\eta^4$ -1,4-dibenzyl-1,3-butadiene; s-cis- $\eta^4$ -1,3-pentadiene; s-cis- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a  $\pi$ -complex as defined herein with the metal.

Most preferably R' is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or phenyl or 2 R' groups (except hydrogen) are linked together, the entire  
15 C<sub>5</sub>R'<sub>4</sub> group thereby being, for example, an indenyl, tetrahydroindenyl, fluorenyl, tetrahydrofluorenyl, or octahydrofluorenyl group.

Highly preferred Y groups are nitrogen or phosphorus containing groups containing a group corresponding to the formula -N(R'')- or -P(R'')- wherein R'' is C<sub>1-10</sub> hydrocarbyl.

20 Most preferred complexes are amidosilane - or amidoalkanediyl complexes.

Most preferred complexes are those wherein M is titanium.

Specific complexes suitable for use in the preparation of the supported catalysts of the present invention are those disclosed in the aforementioned WO 95/00526 and are incorporated herein by reference.

25 A particularly preferred complex for use in the preparation of the supported catalysts of the present invention is (t-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl) dimethyl silanetitanium - $\eta^4$ -1,3-pentadiene.

Suitable cocatalysts for use in the method of the present invention are those typically used with the aforementioned polymerisation catalysts. These include  
30 aluminoxanes such as methyl aluminoxane (MAO), boranes such as tris(pentafluorophenyl) borane and borates. Preferred cocatalysts are ionic compounds comprising a cation and an anion.



The cation of the ionic compound may be selected from the group consisting of acidic cations, carbonium cations, silylium cations, oxonium cations, organometallic cations and cationic oxidizing agents.

5 Suitably preferred cations include trihydrocarbyl substituted ammonium cations eg. triethylammonium, tripropylammonium, tri(n-butyl)ammonium and similar. Also suitable are N,N-dialkylanilinium cations such as N,N-dimethylanilinium cations.

The preferred ionic activators used as cocatalysts are those wherein the cation of the ionic activator comprises a hydrocarbyl substituted ammonium salt and the anion comprises an  
10 aryl substituted borate..

Typical borates suitable as ionic activators include:

triethylammonium tetraphenylborate  
triethylammonium tetraphenylborate,  
tripropylammonium tetraphenylborate,  
15 tri(n-butyl)ammonium tetraphenylborate,  
tri(t-butyl)ammonium tetraphenylborate,  
N,N-dimethylanilinium tetraphenylborate,  
N,N-diethylanilinium tetraphenylborate,  
trimethylammonium tetrakis(pentafluorophenyl) borate,  
20 triethylammonium tetrakis(pentafluorophenyl) borate,  
tripropylammonium tetrakis(pentafluorophenyl) borate,  
tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,  
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,  
N,N-diethylanilinium tetrakis(pentafluorophenyl) borate.

25 A preferred type of activator suitable for use with the metallocene complexes of the present invention comprise ionic compounds comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen.

Suitable activators of this type are described in WO 98/27119 the relevant  
30 portions of which are incorporated herein by reference.

Particular preferred activators of this type are alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates. A particularly preferred activator is

bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate.

With respect to this type of ionic activator, a preferred activator is the reaction product of an alkylammonium tris(pentafluorophenyl)-4-(hydroxyphenyl) borate and an organometallic compound, for example triethylaluminium.

In a preferred method according to the present invention the molar ratio of metallocene complex to ionic activator employed in the method of the present invention may be in the range 1:10000 to 100:1. A preferred range is from 1:5000 to 10:1 and most preferred from 1:10 to 10:1.

It is advantageous in the present invention that the ionic activator is dried before contact with the organometallic compound. This enables lower ratios of organometallic compound to activator to be used without any detrimental effects on activity.

The supported metallocene catalysts of the present invention are most suitable for operation in the gas phase. Gas phase processes for the polymerisation of olefins, especially for the homopolymerisation and the copolymerisation of ethylene and  $\alpha$ -olefins for example 1-butene, 1-hexene, 4-methyl-1-pentene are well known in the art. Particularly preferred gas phase processes are those operating in a fluidised bed. Examples of such processes are described in EP 89691 and EP 699213 the latter being a particularly preferred process for use with the supported catalysts of the present invention.

Particularly preferred polymerisation processes are those comprising the polymerisation of ethylene or the copolymerisation of ethylene and  $\alpha$ -olefins having from 3 to 10 carbon atoms.

Thus according to another aspect of the present invention there is provided a process for the polymerisation of ethylene or the copolymerisation of ethylene and  $\alpha$ -olefins having from 3 to 10 carbon atoms, said process performed under polymerisation conditions in the presence of a supported metallocene catalyst system prepared as hereinbefore described.

The supported catalysts prepared according to the present invention may also be suitable for the preparation of polypropylene, polystyrene, etc.

By use of the method of the present invention a free flowing powder is produced which typically may have a similar particle size to the starting support material. The

resultant supported catalysts are stable at room temperature over extended periods of time and exhibit a less deactivating kinetic profile than similar catalysts prepared without the incorporation of a polymerisable monomer.

5 It is also an advantage of the method of the present invention that supported catalysts may be suitably prepared in a one-pot procedure ie. a preparation carried out without the need for washing steps and typically wherein the contact between the support material, cocatalyst, polymerisation catalyst and monomer is performed in a single reaction vessel.

10 The present invention will now be further illustrated with reference to the following examples:

#### Abbreviations

TEA	triethylaluminium
TiBA	triisobutylaluminium
Ionic Activator A	$[N(H)Me(C_{18-22}H_{37-45})_2][B(C_6F_5)_3(C_6H_4OH)]$
15 Complex A	$(C_5Me_4SiMe_2N^tBu)Ti(\eta^4-1,3-pentadiene)$

#### Example 1

To 30g of Ineos ES70 silica (previously calcined at 500°C for 5 hrs. under nitrogen, pore volume 1.55 ml/g) was added a solution made with 28.13 ml of a hexane solution of TiBA (0.96 mol/l), and 18.38 ml of hexane. The mixture was allowed to  
20 react for 2.5 hrs under agitation then dried under vacuum.

15.06 ml of Ionic Activator A (previously dried by prolonged contact with molecular sieves 4A) was reacted with 2.41 ml of TiBA solution in toluene (0.265mol/l)(molar ratio of TiBA/activator = 0.5 ie. A/B ratio = 0.5)

25 17.47ml of the resultant solution was slowly impregnated (15 min) to the above TiBA treated silica and manually agitated until no lumps were visible.

10,ml of 1-hexene were slowly impregnated (5 min) to the above solution and manually agitated until no lumps were visible followed by holding for 30 mins.

7.16 ml of Complex A in heptane (9.17 %wt) were then slowly added (15 min) and manually agitated until no lumps were visible followed by holding for 1 hr.

30 The catalyst was then dried under reduced pressure to give a loading of [Ti] 40  $\mu$ mol/g.

#### Example 2 Polymerisation Data

269g salt as bed

temperature =  $70^{\circ}\text{C}$

pressure C2 = 6.5 bars

C6/C2 pressure ratio constant at  $4300^{-4}$

5 TEA impregnated silica as scavenger

60 ml. hydrogen added during gas phase composition.

Polymerisation time = 60 min.

Quantity of catalyst injected = 0/101 g

At the end of the polymerisation reaction the polymer produced was separated from the

10 salt by aqueous extraction and drying overnight in an oven.

A slowly decaying activity profile was obtained – after 30 min. of polymerisation the instantaneous catalyst activity was still at 70 g/ghb.

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Claims

1. A method for the preparation of a supported polymerisation catalyst system said method comprising the combination of

- (i) a porous support
- (ii) a polymerisable monomer,
- 5 (iii) a polymerisation catalyst, and
- (iv) a cocatalyst,

*characterised* in that the polymerisable monomer is added to the porous support before addition of one or both of the polymerisation catalyst and the cocatalyst.

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**ABSTRACT**

An improved method for the preparation of a supported polymerisation catalyst system comprises the combination of

- (i) a porous support
- (ii) a polymerisable monomer,
- (iii) a polymerisation catalyst, and
- (iv) a cocatalyst,

*characterised* in that the polymerisable monomer is added to the porous support before addition of one or both of the polymerisation catalyst and the cocatalyst.

The preferred polymerisation catalyst is a metallocene complex and the preferred porous support is silica. The resultant supported catalysts are stable over long periods of time.

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